

## Übersetzung zu der JP 2001-011342 A

### [Detailed Description of the Invention]

#### [0001]

- 5 [Industrial Application] This invention relates to reforming by the surface coating of a pigment particle, and its applicable field.

#### [0002]

[Description of the Prior Art] Reforming by surface coating, such as a pigment particle, is proposed plentifully conventionally, and the distributed stability of a particle, an optical property, a chemistry property, flowability, etc. can improve it now by the various covering approaches. For example, in order to prevent sedimentation and condensation in the enamel of an inorganic pigment, the proposal has carried out surface coating of the inorganic pigment beforehand with the fluoro alkyl group content low-molecular matter (JP,4-208213,A) or oxidization polyethylene (JP,5-132413,A). However, since inorganic and an organic pigment have large specific gravity, it is well known for stable distribution to be difficult, and in ink, even the proposal which secures stable distribution of coloring matter by giving up a pigment and using the color dyeing object of a polymer minute ball as a coloring agent (JP,6-13657,B) exists. In order to prevent that the detailed ultraviolet ray absorbent blended condenses at the charge of makeup, and ultraviolet absorption nature and visible-ray permeability get worse, the thing considered as the spherical resin fine particles which covered the detailed ultraviolet ray absorbent by resin beforehand, and a skin stimulus according to an ultraviolet ray absorbent by doing so, while \*\*\*ing and also preventing chemical deterioration of a component What (JP,8-53568,A) the rough feel by the ultraviolet ray absorbent is lost on the occasion of makeup, and a feeling of use also improves is shown. Although there are a huge number including the above-mentioned example of reforming proposals about the application and surface treatment method of a pigment, there are no thoroughgoing amelioration measures and there is still a deep-rooted thing in the amelioration demand of \*\*, such as the feelings of use including tactile feeling at the time of makeup, in a sex, others, especially the charge of makeup at the time of the distributed stability of a pigment, or a flow. [0003]

[Problem(s) to be Solved by the Invention] Improve many properties of a pigment particle especially a fluidity, the feelings of use including tactile feeling, etc.

#### [0004]

- 40 [Means for Solving the Problem] It expects attaining amelioration of many properties of a pigment particle with the device of surface coating. especially this invention persons were carrying out silica covering of the particle of a zinc oxide, and maintaining the ultraviolet absorption ability of a

zinc oxide, they saw the possible thing of denaturation prevention of the medium by the photochemical catalysis of a zinc oxide, it was in them, and they proposed as a broth and Japanese Patent Application No. No. 370480 [ nine to ]. Furthermore, by making the outermost layer of silica covering into an alkyl denaturation silica, it added to the above-mentioned effectiveness and proposed as an improving [ the fluidity of the constituent containing the pigment concerned or tactile feeling ] \*\*\*\* broth, and Japanese Patent Application No. No. 123468 [ 11 to ]. When aimed at a zinc oxide, titanium oxide, cerium oxide, and a zirconium dioxide, it decided to try about other inorganic pigments and organic pigments of an except. [ finishing / approach / this / seed amelioration / a proposal / in said application already ] Below, this invention is explained at a detail.

[0005] In this invention, the target pigment is an inorganic and organic pigment except a zinc oxide, titanium oxide, cerium oxide, and a zirconium dioxide. Pigments are the fine particles containing a usually detailed primary particle, the aggregated particle which is the floc, or the big and rough particle which they condensed further, and are insolubility and non-reactivity at the solvent object with which a pigment contacts at the time of use. The pigment in this invention is not concerned with the fine-particles configuration, and a color tone is not asked for the pigment of the grain size usually used as a coloring agent.

[0006] The pigment which can be carried out by this invention is the metallic oxide illustrated with various kinds of iron oxides, such as red ocher, the rare earth oxide which is a fluorescent material, the chrome yellow, an alumina, etc. The pigment of the metallic-oxide system which is except a zinc oxide, titanium oxide, cerium oxide, and a zirconium dioxide, The metallic-compounds pigment illustrated in titanium black, titan yellow, ultramarine blue, cobalt blue, etc., Carbon black and a phthalocyanine system, the Indanthrene system, an azo system, the Quinacridone system, Organic pigments, the lake-sized colors, such as a dioxazine system, the Anthraquinone system, an indigo system, a thioindigo system, an azomethine system, a perylene system, a peri non system, and an isoindolinone system, are inorganic, a pearl pigment of the shape of an organic scale, etc. further. It is the compound more specifically indicated by the handbooks of the technical fields concerned, such as a pigment handbook, and cosmetics, a pharmaceutical preparation raw material handbook.

[0007] Homogeneity distribution of a pigment and the stability of distribution from which neither sedimentation nor condensation takes place over a long period of time are mentioned as a trouble in pigment use. Many grinding of a pigment and mechanical energies of kneading are required for uniform distribution, since it is obliged to concomitant use of a dispersant for uniform and stable distribution, the viscosity of a system and other properties change and there is a trouble that excessive adjustment is needed. Al-

though it becomes easy to carry out distribution uniform [ the pigment which carried out surface coating by the silica beforehand ], and stable and the problem of the skin stimulus and color change by direct contact of a pigment is solved, in the medium by which the inside of an oleophilic medium, an oleophilic medium, and a hydrophilic medium coexist, it becomes [ be / it / under / hydrophilic medium / difference / a fluid fall or rough tactile feeling ] remarkable and is dissatisfied. Also when it blends with the cake makeup of cosmetics, there is tactile feeling the bottom coarsely, and since mileage is bad, it is dissatisfied. As a result of inquiring that these troubles should be solved, a header and this invention were reached [ that a trouble is solvable and ] by covering further with an alkyl denaturation silica the pigment which carried out surface coating by the silica.

[0008] The pigment particle concerned of one of the descriptions of the above thing to this invention is silica covering carrying out a inner layer and carrying out surface coating of the outer layer by two-layer [ of alkyl denaturation silica covering ]. Such covering is realizable by performing the sol-gel reaction of tetra-alkoxysilane in the liquefied medium which for example, the pigment particle is distributing, forming a silica layer, and forming an alkyl denaturation silica layer by subsequently performing the sol-gel reaction of alkyl denaturation alkoxysilane. If a silica layer and an alkyl denaturation silica layer are the rates of 20-80:80-20 in a weight ratio and the amount of covering is the 5-% of the weight or more 100 or less % of the weight of range of the pigment particle of a basis, it can attain the purpose of this invention. Effectiveness saturates and is meaningless, if effectiveness decreases more and the amount of covering is excessive, when there are few amounts of covering. In order to attain the purpose of this invention certainly for various applications, the amount of covering is suitable for 20-% of the weight or more 60 or less % of the weight of the range. Since a silica layer and an alkyl denaturation silica layer have the part which is different from each other in the effectiveness, they are above-mentioned within the limits, and should just choose the rate according to an application. In addition, although the pigment with which surface coating of the inner layer was carried out by two-layer [ of alkyl denaturation silica covering and silica covering of an outer layer ] can be similarly realized when covering of an inside-and-outside layer is contrary to the above namely, this inversion covering pigment is not inferior and desirable in a fluidity or tactile feeling.

[0009] As one of the approaches which manufactures the coated particle of this invention, application of a sol-gel reaction is possible. A sol-gel reaction can produce the class of the start raw material, and products various with the device of the reaction approach. Those basic principles and applications are described in the gross in the Sumio Sakuhana work "science of a sol-gel method" (July 5, 1988 publication, company issue of the AGUNE

\*\* style). Among the liquefied medium by which water exists, it condenses it and it forms a Si-O-Si radical while alkoxy silane hydrolyzes and Si-OH radical generates the sol-gel reaction of the alkoxy silane applied by this invention. In inner layer covering formation of this invention, since tetra-  
5 alkoxy silane is used as a start raw material, if a reactant becomes sol-like and condensation progresses further in the midcourse phase of a condensation reaction, the molar fraction of a Si-O-Si radical will increase, and it will become solid-state gel, i.e., a silica. In a sol condition, if a fine-  
10 particles particle coexists in a system, when the surface characteristic and the speed of advance of a sol-gel reaction are suitable, it will stick to a sol on a fine-particles particle front face, and gelation will advance there. If adsorption on the fine-particles particle front face of a sol does not take place, surface coating of a particle is not made, a gelation reaction is too quick, and surface coating is substantially impossible also when the process  
15 in which gel adsorbs is unrealizable. It is suitable for setting the front face of a pigment particle fortunately to this invention, adsorbing a sol at things, and gel depositing. Therefore, if the distributed condition of a pigment particle and the rate of a sol-gel reaction can be chosen proper, it will become possible to attain the purpose of this invention. The alkyl denaturation al-  
20 koxysilane expressed with (\*\* 1) also follows the same process as the above, when several x of alkyl group R' is less than two, and it forms an alkyl denaturation silica.  
[0010] The alkyl denaturation alkoxy silane used as starting material of outer layer covering by the manufacture approach of this invention is a com-  
25 pound expressed with the following general formula.  
[0011]  
[Formula 1]  $R'XSi(OR)4-X$  : However, R and R' is the same or one to C3 different alkyl.  
[0012] In an upper-type compound, although x is 1, the compound whose x is 2 is being mixed to this, and the case where the whole average is less than two is included. Moreover, also when a part or all are those low-grade polymers, it contains. When R and R' is higher-class alkyl, it is unsuitable at the same reason as the preceding clause. In addition, although it can carry out also when R' is various kinds of perfluoro radicals, from the purpose  
30 of this invention, it is disadvantageous for economical efficiency and equi-  
35 valent to superfluous quality.  
[0013] The tetra-alkoxy silane used as starting material of inner layer covering by the manufacture approach of this invention is a compound expressed with the following general formula.  
[0014]  
[Formula 2]  $Si(OR)4$ ; however R are C1 - 3 alkyls.  
[0015] Its reactivity becomes low and is unsuitable, although R of an upper type can be carried out even when this is higher-class alkyl, although it is  
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methyl, ethyl, propyl, and isopropyl. The tetra-alkoxysilane specified by the upper formula may contain the low-grade polymer, or all may be low-grade polymers. Although any of one to C<sub>3</sub> alkyl are sufficient as R, in the case of the ethyl which a rate of reaction tends to control so that covering can carry out to homogeneity more by the mean (i.e., a tetra-ethoxy silane), it is suitable if it says by force. However, the difference which it was at the time is not in one to C<sub>3</sub> alkyl.

[0016] In this invention, although a sol-gel reaction is applied as the covering approach of a pigment particle, tetra-alkoxysilane and alkyl denaturation alkoxy silane which are starting material are dissolved, and the mixture of water and a water-soluble organic solvent is used as a reaction medium so that uniform covering may be possible. On the other hand, since a pigment particle is insolubility, if this is not maintained at a good distributed condition, uniform covering cannot do it, and even if it covers the big and rough particle which many pigment particles condensed, it lacks in the fitness as fine particles. Since a pigment particle contains many condensed big and rough particles before use, it is necessary to grind and distribute this in a medium usable as a sol-gel reaction medium under dispersant existence. Since unescapable association by the sol-gel reaction also takes place a pigment particle being covered with advance of a sol-gel reaction, as for the particle with which a reaction is presented, it is desirable to distribute with a particle size smaller than the time of being used as a coloring agent. A dispersant must have at least the dispersion power force in which the condensation or sedimentation of the pigment particle itself except said unescapable association are not caused, to sol-gel reaction termination. And it is required to be the matter which accelerates too much or does not control a sol-gel reaction. When a dispersant fills such engine performance, a coated particle can turn into a desired surface coating pigment particle.

[0017] The alkanolamine salt of the acrylic polymer which copolymerized an acrylic acid and/or methacrylic acid when looked for the dispersant effective in this invention from an above-mentioned viewpoint, N-vinyl-pyrrolidone-N and N-dialkylamino alkyl acrylate copolymer, The dialkyl sulfate of N-vinyl-pyrrolidone-N and N-dialkylamino alkyl acrylate co-polymer, It found out that one sort of the macromolecule dispersant chosen from the group which consists of an N-vinyl-pyrrolidone vinyl acetate co-polymer, polyvinyl-butyral, and methyl-vinyl-ether-dialkyl maleate co-polymer, or one or more sorts were effective. It is unsuitable because of the acid and alkaline, strong matter accelerating too much, or not completing a sol-gel reaction etc., and, also neutrally, neither polyvinyl alcohol nor ethyl cellulose can demonstrate dispersion force by the system of this invention. The effective matter was not able to be found out with the compound which is known as a surface active agent and dispersion force is also likely to have, for example, the various derivatives of a polyoxyethylene. Al-

though a dispersant changes with presentations of the covering reaction medium which is the class and dispersion-medium object of the pigment for covering, the purpose can be attained if it is used to the weight of pigment fine particles in a profile, and the 0.05-% of the weight or more 100 or less % of the weight of range. In the case of an organic system pigment, with an inorganic system pigment, 0.1-% of the weight or more 100 or less % of the weight of the range is suitable for 2.0-% of the weight or more 20 or less % of the weight of the range. In distribution of the pigment fine particles with which a covering reaction is presented, a well-known wet variational method is applicable in the field concerned.

[0018] Although it is having become clear in process of the dispersant pursuit of the preceding clause, and the mixture of water and a water-soluble organic solvent is used as a reaction medium by the approach of this invention, low-grade aliphatic series monohydric alcohol, such as a methanol, ethanol, and isopropyl alcohol, fully demonstrates the dispersion power force of a dispersant as a water-soluble organic solvent, and since the grain size and tactile feeling of a coated particle are good, moreover, it is a desirable solvent. Water-soluble organic solvents, such as a tetrahydrofuran and aliphatic series ketones, are usable, and the description of a coated particle is also weakly inferior in dispersion force as compared with the case of said alcohol. Therefore, the description of the approach of this invention is in the combination of the use and the water-soluble organic solvent of a specific dispersant. More than the amount of the amount of the water used taken to hydrolyze all the alkoxy groups of the alkoxy silane used for a covering reaction is indispensable, and it secures a water-soluble organic solvent and a distributed condition with a conjointly moderate pigment particle in the bottom of dispersant existence, and an amount in which a smooth reaction advances is used for it. If it says generally, the range of 1.5 times to the 15 time weight of the amount of theory required for hydrolysis is suitable. The amount of the water-soluble organic solvent used secures water and a distributed condition with a conjointly moderate pigment particle in the bottom of dispersant existence, it is the amount in which a smooth reaction advances, and if it says generally, they will be used for it from 1.0 times in the range of weight 15 times to a pigment particle. However, the amount of the sum total used of water and a water-soluble organic solvent has desirable within the limits of 3 times to 20 weight twice of pigment fine particles. It is possible to choose some of these-used water and water-soluble organic solvents, and to consider as the aforementioned dispersion-medium object.

[0019] A catalyst is used at the sol-gel reaction in the approach of this invention. Various kinds of acids and bases are known as a reaction catalyst. However, in the acid catalyst like a hydrochloric acid or an acetic acid, although the surface coating of a fine-particles particle is possible, since pre-

cise and uniform covering cannot be performed, it is unsuitable, the achievement of the conversion of raw material alkoxy silane is inadequate, in the sol-gel reaction of the alkyl denaturation alkoxy silane of outer layer covering, a reaction facilitatory effect is also low and, moreover, a difficulty is in the economical efficiency of covering processing. Before many of sols which catalytic activity is too high and are the intermediate products of a sol-gel reaction cover a pigment particle with the base like a potassium hydroxide or ammonia also according to a basic catalyst, it gels by itself, and the product becomes the mixture of the gel of few covering fine particles and silicas of the amount of covering, or a denaturation silica and is more unsuitable than expectation. Although fatty amines are not so remarkable as the case of ammonia, gelation of the sol itself takes place and the invert ratio to the surface coating of raw material alkoxy silane is bad. Although concentration of these basic catalysts was made low and the improvement of an invert ratio was tried, the improvement which should be satisfied could not be attained but it was that the fall of a reaction rate is only conspicuous. As a result of searching for the catalyst which can avoid such a difficulty, in the surface coating approach of this invention, the alkanolamines expressed with the following general formula found out that it was an effective suitable catalyst.

[0020]

[Formula 3] R<sub>3</sub>-XN(R'OH) X; however R of hydrogen, alkyl, and R' are [ alkylene and x ] 1, 2, or 3.

[0021] By the approach of this invention, since mixed liquor with water, a water-soluble organic solvent, especially low-grade fatty alcohol is used as a reaction medium, alkanolamine chooses and uses what carries out the homogeneity dissolution and has moderate catalytic activity for a reaction medium. Although it changes with the mixing ratio of the water in a reaction medium, and a water-soluble organic solvent, or values of x in an upper type, if the alkyl and alkylene of an upper type become four or more carbon numbers, since solubility and catalytic activity will fall, it is unsuitable. Therefore, hydrogen, the alkyl of carbon numbers 1-3, and R' are [ R ] good to use it, choosing from the alkylens of carbon numbers 1-3. It can carry out, also when the values of x are any of 1, 2, 3, i.e., Monod, G, and a thoria RUKANORU amine, and although a difference is in those reaction acceleration nature, covering made into the purpose of this invention by selection of the amount used can be performed. That is, a prompt sol-gel reaction advances that it is controllable and moderately, and the whole quantity of a sol can make with the covering gel of a pigment particle front face. Moreover, both these catalysts are effective in inner layer covering and outer layer covering, and it is possible to use it in common with both processes. The potassium hydroxide and ammonia of point \*\*, or fatty amines solved, and these points were great differences with the case of a

base.

[0022] As a catalyst of the sol-gel reaction in the approach of this invention, suitably as usable alkanolamine Monoethanolamine, diethanolamine, triethanolamine, Dimethyl monoethanolamine, monomethyl diethanolamine, diethyl monoethanolamine, Monoethyl diethanolamine, mono-propanolamine, dipropanolamine, \*\*, such as tripropanolamine, dimethyl mono-propanolamine, and monoethyl dipropanolamine, are mentioned as the example. Since the covering fine particles diethanolamine, monomethyl diethanolamine, monoethyl diethanolamine, etc. especially excelled [ fine particles ] in tactile feeling are obtained, it is suitable. As for the amount of the catalyst used, it is desirable that it is 5-% of the weight or more 30 or less % of the weight of the range to the weight of the whole alkoxy silane used from a viewpoint of \*\*, such as the ease of carrying out of control of a covering reaction and generated tactile feeling of covering fine particles, and 10-% of the weight or more 25 or less % of the weight of especially the range is suitable.

[0023] It is making it distribute, adding a pigment particle and a dispersant first into a part of mixed liquor of water and a water-soluble organic solvent, and grinding a pigment particle even to a moderate grain size with the application of a well-known approach on the occasion of inner layer covering of the pigment particle in this invention, and the dispersion liquid of a pigment particle are prepared. Although it is convenient that it is the same presentation rate as the medium of a sol-gel reaction as for the liquid of a dispersion-medium object, the presentation rate which there is not and was suitable for distribution is not necessarily sufficient as the need. Into the water of a reaction container, and the mixed liquor of a water-soluble organic solvent, the dispersion liquid of tetra-alkoxy silane and a pigment particle are added under stirring, and it mixes. If a catalyst is added and stirring is continued, hydrolysis and condensation of tetra-alkoxy silane will progress and the viscosity of a system will rise with generation of a sol. In a phase until it results here, it is desirable to make reaction temperature into 10-30-degree C ordinary temperature. It is for avoiding generation of the gel which does not participate in covering. The dispersion liquid of a pigment particle may be added in the phase of the sol generation instead of the beginning. Subsequently, if a temperature up is carried out for gelation reaction acceleration and reflux heating at 60-90 degrees C is continued, a gelation reaction will advance reaction intermediate depositing on a pigment particle front face, and the viscosity of a system will fall. If alkyl denaturation alkoxy silane is added as it is to the system of reaction which inner layer covering ended in this way, hydrolysis and condensation of alkyl denaturation alkoxy silane happening and depositing on the covering inner layer front face of a pigment particle through formation of gel, a gelation reaction will advance and an outer layer covering reaction will be

completed. Unlike the first half of inner layer covering performed in ordinary temperature, it is possible also at the temperature beyond ordinary temperature the first half of an outer layer covering reaction. If carry out a resultant a \*\* exception, the catalyst and dispersant of a residual with the  
5 mixed liquor and those simple substances of water and a water-soluble organic solvent are washed, about 120-160-degree C stoving is performed and it subsequently grinds lightly using equipments, such as a pin mill and an atomizer, the covering fine particles made into the purpose of this invention will be obtained. The reaction yield of the alkoxy silane in covering  
10 fine particles is mostly in agreement with the calculated value it is supposed that they converted into the silica or the denaturation silica. Probably, it is an unreacted edge. - Although it is OH, existence of -OR radical, and contribution of the amount of traces of residue powder, in many cases, yield is a 0 - 4% excessive amount of calculated value. Although reducing  
15 these by hot baking is also assumed, since deterioration of the denaturation silica of an outer layer is not avoided at such temperature, there is no need for baking.

[0024] When distributing the two-layer covering pigment particle of this invention in a medium, the description of the coated particle of this invention Homogeneity distribution can be attained more easily than the case of simple monolayer covering, A dispersion-medium object is liquefied, and when after distribution is liquefied, homogeneity distribution is maintained more by stability over a long period of time, Tactile feeling with good liquefied there being no admiration coarsely on the charge of powder makeup  
20 and according to a coated particle with the sufficient mileage of the charge of makeup etc. and a feeling of use are obtained [ excelling in a fluidity, and ], In that it is possible to make high pigment concentration in the charge of makeup, omitting easily the pigment attached to clothes or the skin, and dealing in it, etc., it appears notably.

25 [0025] Since the distribution to a fluid medium is easy for the covering pigment fine particles of this invention, and it excels in the fluidity when a compound is liquefied In order to utilize the property, application in said charge of makeup is begun. Polyethylene resin, Polypropylene resin, polystyrene resin, acrylic resin, polycarbonate resin, Application to the various resin casts illustrated with urethane resin, an alkyd resin, an epoxy resin, melamine resin, or those copolymer resin, It can apply, also when application in the coating and adhesives using those resin or a low polymerization-degree article is possible and they moreover contain additives, such as a color, pigments other than this invention, an ultraviolet ray absorbent, and a plasticizer.  
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40 [0026] An example is given to below and the detail of this invention is more concretely explained to it. All the sections in an example or the example of a comparison are the weight sections. The particle size of covering fine

particles distributed fine particles to the liquid paraffin, and measured them with the laser diffraction type particle-size-distribution measuring device. the ordinary-temperature distribution stability test which carries out the visual judgment of whether evaluation of distributed stability distributes  
5 fine particles into a hydrophobic liquid, seals them in a transparency container, put in ordinary temperature, and sedimentation of fine particles takes place with time amount, and 50-degree C constant temperature -- after putting into an oven on the 1st, it depended to the acceleration distribution stability test which will continue the repetition cycle of standing in ordinary temperature for one day, and carries out the visual judgment of the  
10 existence of sedimentation.

[0027]

[Example 1] It was made to distribute, teaching the agglomerated powder object 240.0 section of ferrous oxide (red ocher) to a bead mill, and grinding it with the 40.0% ethanol solution 96.0 section of the isopropanolamine salt (whenever [ neutralization ] 75%) of the acrylic-acid denaturation acrylic resin which is a dispersant, and the same weight mixed liquor 464.0 section of isopropanol and water which is a medium. The tetra-ethoxy silane 177 section and the isopropanol 140 section were taught to the dropping equipment of liquid, the reflux condenser, the stirrer, and the reactor that has external heating apparatus, and it was dropped at the bottom of room temperature stirring, having applied [ of the dispersion liquid of said red ocher / 400 ] them for 10 minutes, stirring was continued for a while, and it considered as uniform dispersion liquid. Subsequently, while being  
20 dropped at the bottom of room temperature stirring, having covered [ which consists of the diethanolamine 36 section and the water 200 section ] it for 30 minutes and continuing stirring to the pan for 40 minutes, the viscosity of a system rose and solation of a silane advanced. Heat tracing raised reaction temperature and it kept at 80 degrees C. It gelled a sol sticking to a red ocher particle in 30 minutes, and the viscosity of a system fell.  
25 Since it fell again after the viscosity of a system increased on the way when the reaction agent which consists of the monomethyl trimethoxysilane 33.0 section and the isopropanol 20 section was added and stirring was continued for 60 minutes at 80 degrees C, the reaction was ended. The reactant  
30 was carried out the after [ cooling ] \*\* exception, was rinsed, and removed the solvent, the dispersant, and the catalyst. The yield of the 120-degree C covering fine particles after desiccation was the 188.0 sections. This is substantially equal to the weight 186.3 section when assuming that the whole quantity of silanes converted into the silica and the methyl denaturation  
35 silica, and covered red ocher. Therefore, the presentations of covering-on count fine particles are 64.5 % of the weight of red ocher, 27.0 % of the weight of silicas, and 8.5 % of the weight of methyl denaturation silicas, and the rate of an enveloping layer is 35.5 % of the weight. The obtained  
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covering fine particles were ground for 20 seconds using the impact type pulverizer. The covering fine-particles particle size after grinding was distributed among 0.05 to 3 micrometers, and mean particle diameter was 0.5 micrometers.

5 [0028]

[The example 1 of a comparison] Like the example 1, outer layer covering by monomethyl trimethoxysilane was not carried out, but only the inner layer covering reaction increased the quantity of a tetra-ethoxy silane, and the sol-gel reaction was performed. Covering is quantitative and obtained 10 65.0 % of the weight of red ocher, and the silica covering red ocher of 35.0 % of the weight of silicas. The grain size and particle size distribution after grinding were also equivalent to the case of an example 1.

[0029]

[The example 2 of a comparison] Like the example 1, without carrying out 15 inner layer covering by the tetra-ethoxy silane, the quantity of monomethyl trimethoxysilane was increased by the reaction condition of inner layer covering, and the sol-gel reaction was performed. Covering is quantitative and obtained 66.0 % of the weight of red ocher, and the methyl denaturation 20 silica covering red ocher of 34.0 % of the weight of methyl denaturation silicas. The grain size and particle size distribution after grinding were also equivalent to the case of an example 1.

[0030]

[Example 2] It floated without sedimenting, when the ground covering red 25 ocher fine particles obtained in the example 1 were sprinkled on the water surface. After one week had floated.

[0031]

[The example 3 of a comparison] When the experiment same about the silica independent covering red ocher fine particles [ finishing / grinding ] obtained in the example 1 of a comparison for the comparison as an example 30 2 was conducted on the example 2, fine particles sedimented. The methyl denaturation silica independent covering red ocher fine particles [ finishing / grinding ] obtained in the example 2 of a comparison floated without sedimenting. The red ocher fine particles of the origin which is not covered sedimented.

35 [0032]

[Example 3] The three sections of the ground covering red ocher fine particles obtained in the example 1 were kneaded with the ten sections each of castor oil, a liquid paraffin, and squalane, and were considered as the paste. Any paste was excellent in the fluidity, and it was smooth gravity flow so 40 that the yarn which continued when the rod immersed in the paste was taken up on the paste might be pulled. It turned out [ of these hydrophobic matter and familiarity of these fine particles ] that it is [ a thing ] good.

[0033]

- [The example 4 of a comparison] Although behavior equivalent to an example 3 was shown when the same experiment as an example 3 was conducted by the methyl denaturation silica independent covering red ocher fine particles [ finishing / grinding ] obtained in the example 2 of a comparison for the example 3 and the comparison It fell by the sensibility which did not come to pull the yarn with which it continued in any case in the ground covering red ocher fine particles obtained in the example 1 of a comparison, and the original red ocher fine particles which are not covered, and carried out plasmotomy massive and which was made into BOTE-BOTE, and there was no fluidity.
- [0034]
- [Example 4] The homomixer was used for the 100 sections each of castor oil and a liquid paraffin, the three sections of the ground covering red ocher fine particles obtained in the example 1 were distributed separately, and the ordinary temperature distribution stability test for three months and the acceleration distribution stability test of 8 cycles were presented with the both, respectively. All maintained the good distributed condition and sedimentation or condensation of fine particles were not accepted.
- [0035]
- [The example 5 of a comparison] Although fine particles showed behavior equivalent to an example 4 when the same experiment as an example 4 was conducted by the methyl denaturation silica independent covering red ocher fine particles [ finishing / grinding ] obtained in the example 2 of a comparison for the example 4 and the comparison In the case of the ground covering red ocher fine particles obtained in the example 1 of a comparison, before or after one month, some fine particles sedimented and the film of a transparent supernatant was accepted by the acceleration distribution stability test with the ordinary temperature distribution stability test at the time of four-cycle termination. In the red ocher fine particles of the origin which is not covered, by the ordinary temperature distribution stability test, in any case, it became trustworthy [ at the time of 1 cycle termination / flocking settling of fine particles ] in an acceleration distribution stability test on the 2nd, and it got worse further after that.
- [0036]
- [Example 5] O/W emulsification mold foundation was created by the following combination using the covering fine particles of this invention. That is, the bentonite 0.5 section, the monostearin acid polyoxyethylene sorbitan 0.7 section, the triethanolamine 1.0 section, the propylene glycol 10.0 section, and the purified water 56.4 section were used as aqueous phase, and combination used the stearin acid 3.0 section, the iso hexadecyl alcohol 7.0 section, the glyceryl monostearate 2.0 section, the liquefied lanolin 2.0 section, the liquid paraffin 8.0 section, the antiseptics 0.05 section, and the perfume 0.05 section for the ground covering red ocher fine-particles 0.7

section and the talc 3.0 section which were obtained in the example 1 as fine particles as an oil phase. The creation procedure distributed the bentonite to propylene glycol first, and it carried out homogeneity mixing of the aqueous phase by the homomixer at 70 degrees C, adding purified water and the remaining aquosity components subsequently to this one by one, and it was made it to carry out addition distribution under stirring of the fine-particles component beforehand mixed to this. Under the present circumstances, covering red ocher fine particles were distributed easily and promptly. Furthermore, an oil phase is added at the time of heat, emulsification distribution was carried out, and the perfume after cooling was added. On the occasion of makeup, the obtained foundation had a lubricative property and good tactile feeling, and showed the good result with a feeling of transparency. When the acceleration distribution soundness test was presented, as for sedimentation or condensation of phase separation or covering red ocher fine particles, 45 cycles after was not accepted.

[0037]

[The example 6 of a comparison] For the comparison, the same experiment as an example 5 was conducted on the example 5 using the silica independent covering red ocher fine particles [ finishing / grinding ] obtained in the example 1 of a comparison. The sensibility which is rough on the occasion of makeup carried out the charge of makeup which the mixing time in the homomixer which results in homogeneity distribution took 60% for the excess as compared with the case of an example 5 when carrying out addition distribution of the fine-particles component, and was obtained, and it was the required dissatisfied thing of amelioration a little more in respect of mileage. Sedimentation or condensation of covering oxidization red ocher were not accepted after 45 cycles by the acceleration distribution soundness test.

[0038]

[Example 6] Homogeneity mixing of the ground covering red ocher fine-particles 45.0 section obtained in the example 1, the talc 44.9 section, the starch 2.0 section, the magnesium stearate 3.0 section, the liquid paraffin 3.0 section, the myristic-acid isopropyl 2.0 section, the antiseptics 0.05 section, and the perfume 0.05 section was carried out, coarse grain was excepted by the screen after grinding, and compression molding was carried out at the inside pan. On the occasion of makeup, the obtained powder foundation had a lubricative property and good tactile feeling, and showed the good result with a feeling of transparency.

[0039]

[The example 7 of a comparison] For the comparison, the same experiment as an example 6 was conducted on the example 6 using the silica independent covering red ocher fine particles [ finishing / grinding ] obtained in the example 1 of a comparison. The obtained charge of makeup was inferior to

the case of an example 6 in respect of having sensibility which is rough on the occasion of makeup, and mileage.

[0040]

5 [Example 7] The polystyrene resin pellet 100 section and the ground covering red ocher fine-particles 2 section obtained in the example 1 were mixed, and extrusion molding was carried out with the melting extruder at the shape of a strand. When the strand was turned off and observed to the flake, fine particles were distributed to homogeneity in the strand.

[0041]

10 [The example 8 of a comparison] When the same experiment as an example 7 was conducted on the example 7 using the silica independent covering red ocher fine particles [ finishing / grinding ] obtained in the example 1 of a comparison for the comparison, although fine particles were distributed and made in general into homogeneity into the strand, the pigment 15 fine-particles particle which exceeds 10 micrometers in some places was accepted. Moreover, when the red ocher of the origin which is not covered was used, there is a pigment fine-particles particle which exceeds 10 micrometers by the maldistribution plentifully, and, as for the strand, whenever [ coloring ] was changed in the direction of extrusion.

20 [0042]

25 [Example 8] It was made to distribute, teaching the agglomerated powder object 240.0 section of hydroxylation ferrous oxide (Synthetic Ochre) to a bead mill, and grinding it with the 35.0% ethanol solution 96.0 section of the copolymer of N-vinyl-pyrrolidone [ which is a dispersant ], N, and N-dialkylamino alkyl acrylate, and the same weight mixed liquor 464.0 section of isopropanol and water which is a medium. The tetra-ethoxy silane 177 section and the isopropanol 140 section were taught to the reactor, and it was dropped at the bottom of room temperature stirring, having applied [ of the dispersion liquid of said Synthetic Ochre / 400 ] them for 10 minutes, stirring was continued for a while, and it considered as uniform dispersion liquid. Subsequently, it is dropped at the bottom of room temperature stirring, covering [ which consists of the monoethanolamine 36 section and the water 200 section ] it for 30 minutes, and solation was advanced for stirring continuously [ the pan / for 40 minutes ]. Heat tracing raised reaction temperature to 80 degrees C, and the sol was made to gel for 30 minutes. The reaction agent which consists of the monomethyl trimethoxysilane 33.0 section and the isopropanol 20 section was added, stirring was continued for 60 minutes at 80 degrees C, and the sol-gel reaction was performed. The reactant was carried out the after [ cooling ] \*\* exception, was rinsed, and removed the solvent, the dispersant, and the catalyst. The yield of the 120-degree C covering fine particles after desiccation was the 189.5 sections. This is substantially equal to the weight 186.3 section when assuming that the whole quantity of silanes converted into the silica and the

methyl denaturation silica, and covered Synthetic Ochre. Therefore, the presentations of covering-on count fine particles are 64.5 % of the weight of carbon black, 27.0 % of the weight of silicas, and 8.5 % of the weight of methyl denaturation silicas, and the rate of an enveloping layer is 35.5 % of the weight. The impact type pulverizer ground the obtained covering fine particles for 20 seconds. The covering fine-particles particle size after grinding was distributed among 0.1 to 10 micrometers, and mean particle diameter was 2.5 micrometers. The obtained ground covering carbon black fine particles are used. The water surface spraying float test of an example 5, the paste fluidity test of an example 3, the distribution-among oil soundness test of an example 4, the emulsification mold foundation prototype trial of an example 5, When the powder foundation prototype trial of an example 6 and the trial equivalent to each trial of the resin melting kneading cupping test of an example 7 were performed, like the case of the 10 ground covering red ocher fine particles obtained in the example 1, the engine performance improved rather than the elegance for a comparison, and the satisfying good result was obtained.

[0043]

[Example 9] The carbon black (furnace black) 240.0 section is taught to a 20 bead mill with the 15.0% ethanol solution 400.0 of a dispersant polyvinyl butyral section, and the ethanol 560.0 section which is a medium, and it was made to distribute, grinding carbon black. The tetra-ethoxy silane 169.5 section and the isopropanol 100.0 section were taught to the reactor, and it was dropped at the bottom of room temperature stirring, having applied [ of the aforementioned carbon black dispersion liquid / 600.0 ] them 25 for 10 minutes, stirring was continued for a while, and it considered as uniform dispersion liquid. Subsequently, it was dropped at the bottom of room temperature stirring, having covered [ which consists of the diethanolamine 36.0 section and the water 200 section ] it for 30 minutes, and solation was 30 advanced for stirring continuously [ the pan / for 40 minutes ], subsequently to 80 degrees C reaction temperature was raised, and the sol was made to gel for 30 minutes. After being dropped having applied [ water 140 ] it for 15 minutes, the reaction agent which consists of the mono-methyl trimethoxysilane 33.0 section and the isopropanol 20 section was 35 added, stirring was continued for 60 minutes at 80 degrees C, and the sol-gel reaction was performed. The reactant was carried out the after [ cooling ] \*\* exception, was rinsed, and removed the solvent, the dispersant, and the catalyst. The yield of the 120-degree C covering fine particles after desiccation was quantitative, and it was equivalent to the whole quantity of silanes 40 having converted into the silica and the methyl denaturation silica, and having covered carbon black. The presentations of covering fine particles are 64.5 % of the weight of carbon black, 27.0 % of the weight of silicas, and 8.5 % of the weight of methyl denaturation silicas, and the rate of an

enveloping layer is 35.5 % of the weight. The impact type pulverizer ground the obtained covering fine particles for 20 seconds. The covering fine-particles particle size after grinding was distributed among 0.5 to 8 micrometers, and mean particle diameter was 2.5 micrometers. When the 5 trial equivalent to each trial of the water surface spraying float test of an example 2, the paste fluidity test of an example 3, the distribution-among oil stability test of an example 4, and the resin melting kneading cupping test of an example 7 was performed using the obtained ground covering carbon black fine particles, like the case of the ground covering red ochre 10 fine particles obtained in the example 1, the engine performance improved rather than the elegance for a comparison, and the satisfying good result was obtained.

[0044]

15 [Example 10] The HERIN boss pink CN(CI bat red 1)12.0 section is taught to a bead mill with the 15.0% ethanol solution 22.8 of a dispersant polyvinyl butyral section, and the ethanol 65.2 section which is a medium, and it was made to distribute, grinding pigment fine particles. The tetra-ethoxy silane 56.0 section, the isopropanol 360.0 section, and the mica 135.0 section were taught to the reactor, and it was dropped at the bottom of room 20 temperature stirring, having applied [ of the aforementioned red-pigments dispersion liquid / 56.0 ] them for 10 minutes, stirring was continued for a while, and it considered as uniform dispersion liquid. Subsequently, it is dropped at the bottom of room temperature stirring, covering [ which consists of the diethanolamine 16.8 section and the water 22.5 section ] it for 25 30 minutes, and solation was advanced for stirring continuously [ the pan / for 40 minutes ]. Heat tracing raised reaction temperature and the sol was made to gel for 30 minutes. Subsequently, after being dropped having applied [ water 270 ] it for 15 minutes, the reaction agent which consists of the monomethyl trimethoxysilane 45.0 section and the ethanol 25 section 30 was added, stirring was continued for 60 more minutes, and the sol-gel reaction was performed. The reactant was carried out the after [ cooling ] \*\* exception, and ethanol and water washed it, and it removed the solvent, the dispersant, and the catalyst. The yield of the 120-degree C covering fine 35 particles after desiccation is quantitative, and it was equivalent to the whole quantity of silanes having converted to the silica and the methyl denaturation silica. The impact type pulverizer ground the obtained covering fine particles for 10 seconds. The mean particle diameter of the covering fine particles after grinding was 10.5 micrometers. It was admitted that these fine particles were the structure where a pigment and the complex of a mica were covered with silicas. The good result the engine performance improves rather than the elegance for a comparison like [ when a trial equivalent to each trial of the water-surface spraying float test of an example 2, the paste fluidity test of an example 3, the distribution-among oil sound-

ness test of an example 4, the emulsification mold foundation prototype trial of an example 5, and a powder foundation prototype trial of an example 6 is performed ] the case of the ground covering red-ocher fine particles obtained in the example 1, and it can be satisfied with fine particles [ finishing / grinding ] of a good result obtained.

[0045]

[Example 11] The copper-phthalocyanine-blue (CI pigment blue 15) fine-particles 240.0 section is taught to a bead mill with the 15.0% ethanol solution 400.0 of a dispersant polyvinyl butyral section, and the ethanol 560.0 section, and it was made to distribute, grinding copper-phthalocyanine-blue fine particles. The tetra-ethoxy silane 169.5 section and the isopropanol 100 section were taught to the reactor, and it was dropped at the bottom of room temperature stirring, having applied [ of the aforementioned copper-phthalocyanine-blue dispersion liquid / 600.0 ] them for 10 minutes, stirring was continued for a while, and it considered as uniform dispersion liquid. Subsequently, it is dropped at the bottom of room temperature stirring, covering [ which consists of the diethanolamine 36 section and the water 200 section ] it for 30 minutes, and solation was advanced for stirring continuously [ the pan / for 40 minutes ]. Heat tracing raised reaction temperature and the sol was made to gel for 30 minutes. After being dropped having applied [ water 140 ] it for 10 minutes, the reaction agent which consists of the monomethyl trimethoxysilane 33.0 section and the isopropanol 20 section was added, stirring was continued for 60 more minutes, and the sol-gel reaction was performed. The reactant was carried out the after [ cooling ] \*\* exception, and ethanol and water washed it, and it removed the solvent, the dispersant, and the catalyst. The yield of the 120-degree C covering fine particles after desiccation is quantitative, and it was equivalent to the whole quantity of silanes having converted into the silica and the methyl denaturation silica, and having covered the copper phthalocyanine blue. The impact type pulverizer ground the obtained covering fine particles for 20 seconds. The covering fine-particles particle size after grinding was distributed among 0.5 to 8 micrometers, and mean particle diameter was 2.6 micrometers. When the trial equivalent to the water-surface spraying float test of an example 2, the paste fluidity test of an example 3, the distribution-among oil soundness test of an example 4, the emulsification mold foundation prototype trial of an example 5, and the powder foundation prototype trial of an example 6 was performed by the obtained ground covering copper-phthalocyanine-blue fine particles, the engine performance improved rather than the elegance for a comparison, and a satisfying good result obtained like the case of the ground covering red-ocher fine particles obtained in the example 1.

[0046]

[Example 12] It changed to the copper-phthalocyanine-blue fine particles

in an example 11, and the approach of an example 11 was repeated per each using one sort of the following pigment or the lake-ized color.

Brilliant Fast Scarlet (CI pigment red 24)

Bench gin yellow G (CI pigment yellow 14)

5 Phthalocyanine Green (CI pigment Green 7)

Litholrubin BCA (CI pigment red 57-1)

Two-layer covering quantitative in any case could be performed, and the good result the engine performance improves rather than the elegance for a comparison like the case of an example 11, and it can be satisfied with the 10 performance test of covering fine particles of the good result was obtained.  
[0047]

[The example 9 of a comparison] The class of dispersant was changed to Na salt of acrylic-acid copolymerization acrylic resin, and the approach of 15 an example 1 was repeated. Condensation of a red ocher particle advanced to sol-gel reaction time, and the silica gel without regards to covering generated the part. By fine particles after after grinding is the fine particles of tactile feeling the bottom coarsely because of a big and rough particle and removes a big and rough particle Although the trial equivalent to the paste 20 fluidity test of an example 3, the distribution-among oil soundness test of an example 4, the emulsification mold foundation prototype trial of an example 5, and the powder foundation prototype trial of an example 6 was carried out There was little improvement width of face of the paste fluidity by covering or distribution-among oil stability, and an improvement of a 25 feeling of a rough deposit or mileage was not accepted as a charge of makeup.  
[0048]

[The example 10 of a comparison] The class of catalyst was changed to ammonia from diethanolamine, and the aqueous ammonia 10.4 section was 30 diluted with the water of the 200 sections 28%, it used, and the approach of an example 11 was repeated. Blinding happened to the filter paper after a reaction, and the \*\* exception of a reactant was not made to it. When the solid content obtained by carrying out evaporation to dryness was observed, it turned out that the copper-phthalocyanine-blue particle of covering imperfection and the silica gel particle are intermingled. By the 35 performance test, an improvement of a feeling of a rough deposit or mileage was not accepted as the paste fluidity of these fine particles, distribution-among oil stability, and a charge of makeup.  
[0049]

[The example 11 of a comparison] The class of catalyst was changed to 40 triethylamine and the approach of an example 10 was repeated. When the obtained fine particles were observed, it turned out that the silica gel particle is intermingled. By the performance test, the improvement of a feeling of a rough deposit or mileage was not substantially accepted as the paste

fluidity of these fine particles, distribution-among oil stability, and a charge of makeup.

[0050]

5 [Effect of the Invention] The distribution to a fluid medium is easy for the covering pigment fine particles of this invention, and since dispersed liquid is excellent in a fluidity and moreover has long-term distribution stability, it applies to the charge of makeup, a coating, adhesives, a resin cast, etc. and is useful. It is suitable as a coloring agent in the use on use, such as there being especially no feeling of a rough deposit, and being easy to be  
10 mileage, to the charge of makeup. Moreover, according to the approach of this invention, the useful covering pigment fine particles which fill the aforementioned engine performance to coincidence can be manufactured.

15

[Claim(s)]

- [Claim 1] The denaturation silica covering pigment particle characterized by covering with the 5-% of the weight or more silica [ 100 or less % of the weight of ] system matter the front face of the pigment particle chosen  
5 from the group which consists of the inorganic pigment and organic pigment except a zinc oxide, titanium oxide, cerium oxide, and a zirconium dioxide, and for the inner layer of an enveloping layer being a silica, and an outer layer being an alkyl denaturation silica.
- [Claim 2] The constituent characterized by blending the denaturation silica covering pigment particle of claim 1 with the charge of makeup, a coating, adhesives, or a resin cast.  
10
- [Claim 3] the pigment particle chosen from the group which consists of the inorganic pigment and organic pigment except a zinc oxide, titanium oxide, cerium oxide, and a zirconium dioxide -- a dispersant -- using -- an organic  
15 dispersion medium -- the manufacture approach of the denaturation silica covering pigment particle characterized by distributing the inside of the body, carrying out the sol-gel reaction of the tetra-alkoxysilane in this dispersed system, and subsequently carrying out the sol-gel reaction of the alkyl alkoxysilane in this dispersed system.
- 20 [Claim 4] The manufacture approach of claim 3 characterized by being a kind of the macromolecule dispersant chosen from the group which a dispersant becomes from a dialkyl sulfate [ of alkanolamine salt / of an acrylic acid and/or a methacrylic acid copolymer /, N-vinyl-pyrrolidone-N, and N-dialkylamino alkyl acrylate copolymer, N-vinyl-pyrrolidone-N, and N-dialkylamino alkyl acrylate copolymer ], N-vinyl-pyrrolidone vinyl acetate copolymer, polyvinyl-butylal, and methyl-vinyl-ether-dialkyl maleate copolymer in the approach of claim 3, or more than a kind.  
25
- [Claim 5] The manufacture approach of claim 3 characterized by using alkanolamines as a reaction catalyst in the approach of claim 3.